# Nonlinear Dielectric Properties of Cyanoethylated 0-(2, 3-Dihydroxypropyl) cellulose in Ult r a L ow Frequency Region in Ult r a L ow Frequency Region (Commemoration Issue Dedicated to Professor Tetsuya HANAI On the Occasion of His Retirement)



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# Nonlinear Dielectric Properties of Cyanoethylated O-(2, 3-Dihydroxypropyl)cellulose in Ultra Low Frequency Region

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Many investigations[1] for dielectric properties of polymeric liquid crystal have been carried out in an audio and radio frequency region. It is known that some relaxation processes take place in ultra low frequency region far below 1 Hz. In the course of measurement of dielectric permittivity for a liquid crystalline polymer cyanoethylated O-(2, 3-dihydroxypropyl)cellulose (CN-DHPC), an obvious deviation from the linear property was observed in ultra low frequency region. It may be expected that liquid crystalline polymer shows nonlinear dielectric properties in such ultra low frequency region. In order to study linear and nonlinear dielectric behavior of polymer in low frequency region, it is necessary to construct a suitable measuring system. In this communication, an apparatus for measuring dielectric properties in ulta low frequency region has been constructed and preliminary data are reported, demonstrating that CN-DHPC exhibits remarkable nonlinear dielectric properties.

## Measuring System

The block diagram of the system to measure linear and nonlinear dielectric susceptibilities in frequency domain is shown in Fig. 1. The function generator supplies the gate (in Fig. 1.) with a continuous wave of sinusoidal voltage $V(t)$ as

$$V(t) = V_o \mathrm{Im}[\exp(j\omega t)], \tag{1}$$

where $V_o$ is an amplitude of voltage, $\omega$ $(=2\pi f)$ an angular frequency, $t$ time and $j=\sqrt{-1}$. To determine time, the TTL signal synchronous to sine wave is also supplied to the gate and to the personal computer. The gate is opened or closed at the time when the sign of voltage changes from negative to positive. The gate tells the computer its open interval. Timing charts and detail of the gate circuits are illustrated in Fig. 2. The sample in dielectric cell is applied with a voltage of Eq. (1) when the gate is open and a response electric current flows into a current-to-voltage converter(I-V converter). The system constructed here measures an electric current not a charge, because a time

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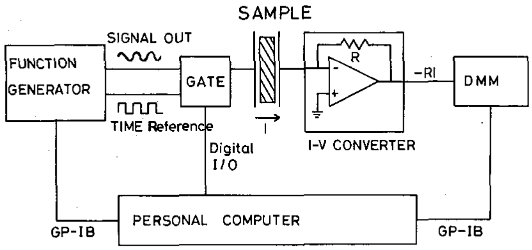


Fig. 1. Block diagrams of the measuring system.
FUNCTION GENERATOR: Hewlett packard 3325B Synthesizer/Function Generator with High Voltage Output.
GATE: Electrical curcuits of the gate is shown in Fig.2.
I-V CONVERTER: AD-549 operational amplifiers were used.
DMM: Keithley 196 model
PERSONAL COMPUTER: EPSON PC-286VS.

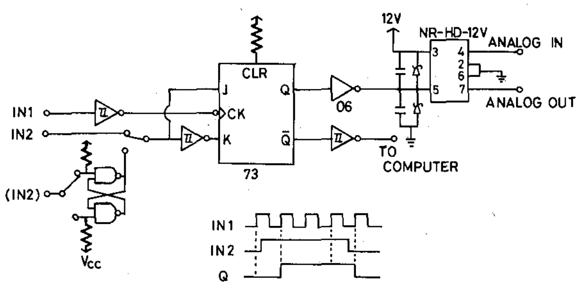


Fig. 2. Electrical curcuits and timing chart of the gate.
IN1: TTL from function generator.
IN2: from computer. (IN2): Manual input.

independent current is possible to flow in nonlinear dielectrics. The voltage proportional to response current serves in a digital multimeter (DMM) of a Keithley 196 model. DMM begins the data acquisition, samples first datum at the time indicated by computer and samples voltages at every increment of computer indication. The Fourier transformation of these data, which DMM has sended to the computer, yields linear and nonlinear permittivities.

### Complex permittivity of n-th order

According to the theory of nonlinear response developed by Nakada[2], response current $I$ resulted from sinusoidal excitation is expressed as

$$I = V_o[Y_1'\sin\omega t + Y_1''\cos\omega t] + V_o^2[Y_2'\sin 2\omega t + Y_2''\cos 2\omega t + Y_2^0] + V_o^3[Y_3'\sin 3\omega t + Y_3''\cos 3\omega t + Y_3^+\sin\omega t + Y_3^{++}\cos\omega t] + \ldots \quad (2)$$

If an approximation of $Y_1' >> V_o^2 Y_3^+$ and $Y_1'' >> V_o^2 Y_3^{++}$ is adopted, Eq.(2) is rewritten to

$$I = I_o + \mathrm{Im}[\sum_{n=1}^{N} Y_n V_o^n \exp(jn\omega t)], \quad (3)$$

where

$$I_o = V_o^2 Y_2^0 \text{ and } Y_n = Y_n' + jY_n'' \ (n=1, 2, \ldots). \tag{4}$$

It should be emphasized that, in nonlinear dielectrics, a current resulted from sinusoidal excitation without dc bias consists of a time independent component. This component depends on an amplitude of voltage. Strictly speaking, the component depends on time for several periods after a change of amplitude and reaches an equilibrium value after a long time. An electric current, in general, can be expressed by using n-th order admittance $Y_n$ as

$$I(\omega, V_o, t) = I_o(\omega, V_o) + \mathrm{Im}[\sum_{n=1}^{N} \mathrm{Y}_n(\omega, V_o) V^n(\omega, V_o, t)] \tag{5}$$

$$= I_o + \mathrm{Im}[\sum_{n=1}^{N} \mathrm{Y}_n \mathrm{V}_o{}^n \exp(jn\omega t)], \tag{5'}$$

where $I_o$ is a time independent component. Since Eq. (3) is identical with Eq. (5'), the coefficient $Y_n$ in Eqs. (3) and (4) can be attributed to n-th order admittance.

The Fourier transformation of the response current determines the admittance as follows,

$$I(t) = I_o + \sum_{n=1}^{N} [a_n \cos(n\omega t) + b_n \sin(n\omega t)],$$

$$I_o = f \int_0^{1/f} I(t) \mathrm{d}t,$$

$$\mathrm{Y}_n'' \mathrm{V}_o^n = \mathrm{a}_n = 2f \int_0^{1/f} \mathrm{I}(t) \cos(n\omega t) \mathrm{d}t, \tag{6}$$

$$Y_n' V_o^n = b_n = 2f \int_0^{1/f} I(t) \sin(n\omega t) \mathrm{d}t. \tag{7}$$

Here $n$-th order complex capacitance $C_n (= C_n' - jC_n'')$ is introduced by definition of

$$Q = C_n V^n, \tag{8}$$

where $Q$ ia a charge.

Sinusoidal excitation of Eq. (1) and differentiation of above equation with time give

$$I = jn\omega C_n V^n.$$

Therefore

$$Y_n = jn\omega C_n, \tag{9}$$

or

$$Y_n' = n\omega C_n'' \text{ and } Y_n'' = n\omega C_n'.$$

Eqs. (3) and (9) and the dimensions of dielectric cell, whose electrode has an area $S$ and a separation $d$ between the other electrode, give the current density $i$ as

$$i = i_o + \mathrm{Im}[\sum_{n=1}^{N} jn\omega \varepsilon_n E_o{}^n \exp(jn\omega t)] \tag{10}$$

where

$$i = I/S,\ i_o = I_o/S,\ E = V/d,\ E_o = V_o/d, \text{ and } \varepsilon_n = C_n d^n/S. \tag{11}$$

We define the coefficient $\varepsilon_n$ in Eq. (10) to be n-th order complex permittivity. Some definition[3] of n-th order complex permittivity $\varepsilon_n$ was given as

$$\varepsilon_n = 1/n!(\partial^n D/\partial E^n)_{E=0}, \tag{12}$$

where $D$ is an electric displacement. The permittivity defined above does not depend on an amplitude of field, though the permittivity defined with Eq. (10) does. Nonlinear dielectric permittivity reflects not only higher order perturbation of thermal motion but also motional mode forced by external field[4]. The permittivity in relation with molecular motion forced by external field depends on field strength. We cannot adopt the definition of Eq. (12). The definition of Eq. (10) can be rewritten in a similar form to Eq. (12) as

$$\varepsilon_n(\omega,E_o) = 1/n!(\partial^n D/\partial E^n)_{E_o=E_o}. \tag{13}$$

**Performance of the measuring system**

The performance of the measuring system was examined by measurements of a nominal 1 MΩ metal film resister and of a nominal 10 nF polystyrene capacitor. The resistance $R$ and phase angle $\phi$ of the nominal 1 MΩ resister measured with the system equipped here are listed in Table 1. Measurement in dc condition with DMM determined the resistance of the resister as 1.001375 MΩ. If the resistance in dc condition is not different from that in low frequency region, the measuring system can measure the 1 MΩ resister within an accuracy of 0.1 % error. Table 2. gives the capacitance, admittance and phase angle of the nominal 10 nF capacitor measured with the measuring system in ultra low frequency region and with a Hewllet Packard 4284A precision LCR meter from 100 Hz to 1 MHz. If the measurement with LCR meter at 10 kHz is precise and the capacitance of the nominal 10 nF capacitor does not depend on frequency, the capacitance measured by the system is accurate within 10 % error

Table 1. Resistance and phase angle of a nominal 1 MΩ resister measured with the measuring system. The measurement in dc condition with a Keithley 196 DMM yields 1.001375 MΩ.

| f/mHz | .999 | 1.999 | 5.001 | 9.998 | 19.98 | 49.99 | 99.57 |
|---|---|---|---|---|---|---|---|
| R/MΩ | 1.00150 | 1.00166 | 1.00180 | 1.00211 | 1.00160 | 1.00082 | 1.00044 |
| $\phi$/deg | −.37 | .026 | .28 | .40 | .78 | 1.74 | 3.1 |

Table 2. Capacitance and admittance of a nominal 10 nF capasitor measured with the measuring system or with a HP 4284A precision LCR meter.

| The measuring system | | | | | | |
|---|---|---|---|---|---|---|
| f/mHz | 1.999 | 5.001 | 9.998 | 19.98 | 49.99 | 99.57 |
| C/nF | 16.1 | 10.2 | 11.1 | 9.3 | 10.8 | 10.3 |
| $\phi$/deg | 86.7 | 88.7 | 89.9 | 89.2 | 90.9 | 91.2 |
| Y/nS | .202 | .320 | .698 | 1.17 | 3.41 | 6.43 |

| Precision LCR meter | | | | | |
|---|---|---|---|---|---|
| f/kHz | .1 | 1 | 10 | 100 | 1000 |
| C/nF | 10.1782 | 10.1757 | 10.1767 | 10.1762 | 10.1962 |
| $\phi$/deg | 90.08 | 90.04 | 90.00 | 89.97 | 89.58 |

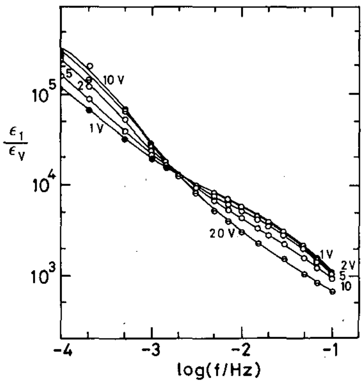


Fig. 3. First order permittivity of CN-DHPC at 302 K against frequency. $\varepsilon_v$ is permittivity of vacuum. Applied voltage was indicated in the figure.

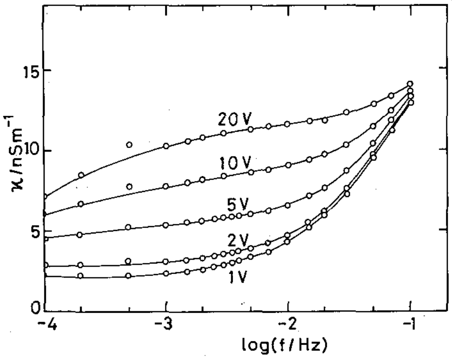


Fig. 4. First order conductivity of CN-DHPC at 302 K against frequency. Applied voltage was indicated in the figure.

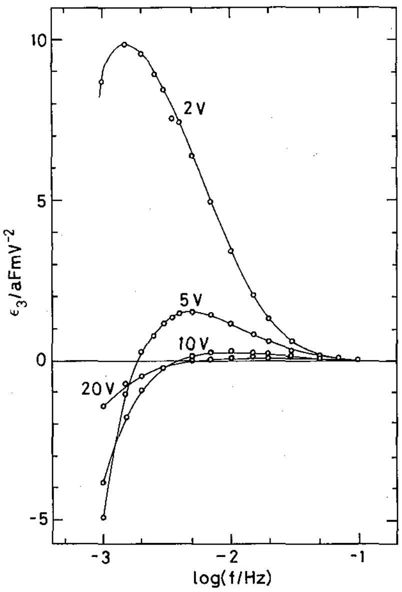


Fig. 5. Third order permittivity of CN-DHPC at 302 K against frequency. Applied voltage was indicated in the figure.

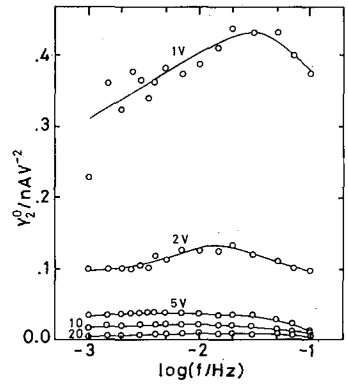


Fig. 6. One of second order admittance $Y_2{}^0$, which causes time independent current, of CN-DHPC at 302 K against frequency. Applied voltage was indicated in the figure.

for an admittance larger than 0.3 nS. The system equipped here seems available to measure linear and nonlinear permittivities.

## Nonlinear permittivity of a polymeric liquid crystal

The sample CN-DHPC was the same as DH-4-CN the notation in previous paper[5]. Dielectric properties of CN-DHPC were measured at the temperature of 302 K in ultra low frequency region of .1-100 mHz with the two-terminal cell, of which area $S$ of electrode surface was $7.85 \times 10^{-5}$ m$^2$ and separation $d$ between electrodes was .0001 m.

Fig. 3. shows relative permittivity in logarithmic scale. Permittivity was very large and increased abnormally at lower frequency. Field dependence of conductivities shown in Fig. 4 suggests a motion forced with external field in mHz region. Extrapolation toward .1-10 Hz region in Fig. 4 suggests a thermally exited motion, which is already noted in previous work[5]. Remarkablly large permittivities of third order $\varepsilon_3$ were observed in CN-DHPC as shown in Fig. 5. Furukawa *et al.*[6] observed a large $\varepsilon_3$ for vinylidenecyanide(VDCN)/vinylacetate(VAc) copolymer in audio frequency region. The $\varepsilon_3$ for CN-DHPC is by no means small in comparison with that for VDCN/VAc copolymer, though it is difficult to compare directly due to measurements at different frequencies. The large $\varepsilon_3$ for CN-DHPC seems to be resulted from the large $\varepsilon_1$ at low frequencies, the low viscosity for liquid crystalline phase, and an active motion of cyanoethyl group enabled by flexible spacers between cyanoethyl group and semi-rigid back bone. The large $\varepsilon_3$ gave a possibility to observe the very small quantity as second order admittance $Y_2^0$ which causes time independent current. Figure 6 illustrates positive $Y_2^0$ against frequency. Figure 6 is one of the experimental proof of Nakada's theory[2]. More extensive and detailed investigation is in progress.

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